Production of fluoridated salt

Summary
Sodium and potassium fluoride are used for the fluoridation of household salt. Addition of fluoride is carried out either by the wet or the dry process. Qualitatively good fluoridated salt can be produced by using either method. In the wet process, a solution of potassium fluoride is mixed homogeneously with the salt. For the dry mixture, only sodium fluoride with a small granule size is suitable. Apart from the mixing methods used by the larger salt manufacturers, there are low-cost solutions for very small producers.

Introduction
Europe stands alongside North and South America and Asia as one of the world’s major salt production areas. In Eastern Europe and Western Europe, annually about 50 million tonnes of salt (sodium chloride) are produced in crystalline form (as evaporated salt, rock salt and sea salt) and brine. Salt is produced by solar evaporation (sea salt), dry underground mining (rock salt) and solution mining (evaporated salt, salt in brine). The total annual consumption of edible salt in Europe is approximately 2.5 million tonnes. Edible salt is used as a carrier for the nutrients iodine, fluorine and folic acid (BURGI & ZIMMERMANN 2005). Industrial production of fluoridated salt started in Switzerland in 1955. Today, household or domestic salt is fluoridated in eight European countries.

Techniques of adding fluorides to salt
The addition of fluorides to salt is either by a wet method or a dry method (BURGI & RUTSHAUSER 1986). Both processes are used in Europe. The quality of fluoridated salt produced by both of these methods is identical. Evaporated salt and sea salt are the types most commonly fluoridated. Normally, the salt is subjected to multiple enrichment. At the same time as fluoridation, the salt is iodised either with iodides or with iodates. In Germany, the basic salt for fluoridation is iodised salt, to which folic acid is also sometimes added.

Fluoridation chemicals
The fluorine chemicals used for salt fluoridation and their important properties are listed in Table I. An important parameter for selection of the fluoridation process is solubility in water. Whereas potassium fluoride is highly soluble in water, sodium fluoride is considerably less soluble. Potassium fluoride is markedly hygroscopic, while sodium fluoride is not. The difference in price between the two fluorides means that at a fluoride addition of 250 mg/kg of salt, the costs of the compound, which is a minor part of the total cost of addition of fluoride to salt, are about three times higher when using potassium fluoride instead of sodium fluoride.
Typical process chain

The typical procedure at the producer of fluoridated salt starts with the crystallisation of the salt (evaporated salt, sea salt), then washing the salt crystals either before or during separation of the salt crystals from the saturated brine by centrifuging in pusher or screen centrifuges and drying the salt with hot air in fluidised bed or rotary drum dryers (Fig. 1). The fine and coarse particles which are created during the crystallisation process are separated out by means of sieves or air separators and used for special purposes. Additives may be added either before the drying process or after grain size classification. Since salt producers in Europe normally also produce edible salt without fluorine or iodine, and extract salt for other purposes as well from the stream of salt leaving the dryer, it is usual to put in the additive after the fluidised bed dryer and screening. The actual point at which the fluoride is added also depends on whether the wet or the dry method is being used. Dry salt fluoridation is only possible when the fluoride is not added until after the stages of drying and screening. Otherwise, because of its small grain size, the fluoride will be removed again from the salt in the dryer exhaust or during the screening.

When the fluoride is added before the dryer, the fluidised bed mixes the fluoride with the salt. When the fluoride is added after screening, an agitator has to be used to achieve homogeneity in the mixture. It is recommended that the fluoride addition is not made until after the drying and screening stages, since the fluoride content in the differently-sized grains varies, and as a result of the separation of fine and coarse particles, it is difficult to maintain the required fluoride content.

The principles of the process in a modern European plant are shown in the flow-chart for the Bad Reichenhall salt refinery (Fig. 2).

Fluoridation of rock salt is generally carried out by adding the fluoride either wet or dry, following on from the usual stages of the mining process of extraction, crushing and screening.

The wet method

In the wet method, an aqueous solution of potassium fluoride is continuously sprayed, at a specific ratio, on salt travelling past on a conveyor belt. The concentration of the solution may vary, but should as far as possible be high, so that the carry-over of water into the dried salt remains low. To achieve the necessary homogeneity, after this the salt is passed through a mixing stage. Mixers are either fluidised bed dryers or continuous agitators. When using batch processing, the potassium fluoride solution is sprayed directly into the batch mixer.

The dry method

For this method, only sodium fluoride is suitable, because the dosage of potassium fluoride cannot be reliably controlled on account of its extreme hygroscopicity. Powdered sodium fluoride is continuously fed by means of a solids dosing apparatus into a continuous mixer or mixed in batches with salt in a batch-mixer. Sodium fluoride with a grain size of 10 to 20 µm is used to achieve a homogeneous product with no tendency to separate out even in the salt package.

Tab. 1 Fluoride chemicals

<table>
<thead>
<tr>
<th></th>
<th>Sodium fluoride</th>
<th>Potassium fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>NaF</td>
<td>KF</td>
</tr>
<tr>
<td>CAS No.</td>
<td>7681-49-4</td>
<td>7789-23-3</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>41.99</td>
<td>58.10</td>
</tr>
<tr>
<td>Solubility (g/100 ml water)</td>
<td>4.0 (15°C)</td>
<td>92.3 (18°C)</td>
</tr>
<tr>
<td>Specific gravity (g/cm³)</td>
<td>2.558</td>
<td>2.48</td>
</tr>
<tr>
<td>Bulk density (kg/l)</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Particle size</td>
<td>10-20 µm</td>
<td>90% &lt; 150 µm</td>
</tr>
<tr>
<td>Water content (%/2 hrs/105°C)</td>
<td>max. 0.1</td>
<td>max. 0.2</td>
</tr>
<tr>
<td>pH value</td>
<td>10.2 (40 g/l)</td>
<td>7–9 (50 g/l)</td>
</tr>
<tr>
<td>Price (euro/kg)</td>
<td>1.50</td>
<td>3.50</td>
</tr>
<tr>
<td>g required per ton salt</td>
<td>552</td>
<td>764.5</td>
</tr>
<tr>
<td>Fluoride costs per ton salt (euro)</td>
<td>0.85</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Fig. 1 Typical process chain during the production of salt with additives
Advantages and disadvantages of the methods

The advantages of the dry method are the lower costs of chemicals and the reduced water carry-over into the salt. The latter has a particularly beneficial effect when packaging the fluoridated salt in that there are less incrustations left behind on the metallic surfaces of the packaging machinery in contact with the salt, which reduces cleaning costs. The disadvantage is that the dry method demands salt with a narrow range of granule sizes – from 0.2 to 0.8 mm. The dry method is unsuitable for coarse salt, since the larger the crystal, the greater the tendency is for the sizes to separate out. Thus, in a packet of salt, one would find the small-grained fluoride powder tending to accumulate on the bottom of the packet. Therefore the wet method is to be recommended for coarse salt.

The wet method is suitable for all ranges of granule size usually found in the household. Salt granules are covered with a layer of potassium fluoride solution in production. This happens irrespective of the granule size. Admittedly, due to their comparatively large surface area, the finer granules take up proportionately more solution than the larger granules. In the wet method, the granular size of the potassium fluoride is of no significance (Milner).

Mixers for salt fluoridation

In batch systems a specific quantity of fluoride is added in liquid or solid form to each batch. The most common batch mixers are:

- **Tumbler mixers**: The simplest type of mixers, which consist of a horizontal rotating drum with or without ribbons.
- **Screw mixers**: A popular mixer is the "Nauta" mixer, a vertical cone mixer, which consists of an inverted cone fitted with circulating screw agitators. The horizontal ribbon blender consists of a rotating shaft fitted with two helical ribbons, which rotate in opposite directions inside a semicircular trough.
- **Paddle mixers**: Well known is the “Lödige” mixer, a horizontal mixer, which bears ploughshares on the rotating shaft.

For the addition of the potassium fluoride solution, spray nozzles are positioned inside a mixer. Simultaneous addition of solutions with iodide or iodate and anti-caking agent is carried out in the same manner. Sodium fluoride is added with a gravimetric feeder.

For continuous systems, the fluoride is added through a volumetric or gravimetric feeder at a rate compatible with the flow rate of the salt to ensure the correct dosage in the salt. Commonly used continuous mixers are:

- **Screw conveyors**: An economical solution which also transports the fluoridated salt to the packaging station.
- **Paddle mixers**: The "Lödige" type can be modified for continuous processing.

For small-scale production of fluoridated salt, simple low-cost mixing equipment can be used. One possibility is hand mixing with the use of a rotary drum unit that works like a cement mixer (Lofti et al. 1996).

Zusammenfassung


Neben den Mischmethoden, die von grossen Salzherstellern praktiziert werden, gibt es auch kostengünstige Lösungen für Kleinhersteller.

Résumé

Pour fluorer des sels domestiques, on utilise du fluorure de sodium et de potassium. Ce faisant, l’addition du fluorure est
réalisée soit par un procédé humide, soit sec. Les deux méthodes permettent d’obtenir des sels fluorés de bonne qualité. Pour ce qui est du procédé humide, une solution aqueuse de fluorure de potassium est mélangée au sel de façon homogène. Pour ce qui est du procédé à sec, seul un fluorure de sodium à grains très fins est bien approprié.
En plus des méthodes de mélange pratiquées par les grands fabricants de sels, il y a aussi des solutions économiques pour les petits fabricants.

References